

SELECTIVE HYDRODESULFURIZATION OF FCC GASOLINE OVER CoMo/Al₂O₃ SULFIDE CATALYSTS

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Introduction

FCC gasoline is one of the major components of motor gasoline. It contains high level of sulfur derived from heavy gas oil and atmospheric residue used as FCC raw materials. FCC gasoline also contains valuable olefins which contribute to the octane number of the motor gasoline. Therefore, the selective hydrodesulfurization which minimizes octane loss is highly desired to meet the severe limitation of sulfur content (1~3). In this study, the selective hydrodesulfurization (HDS) of FCC gasoline over new sulfide catalysts was investigated.

Experimental

Two kinds of FCC gasoline (full-range and 60 °C +) were used here. The properties of them are summarized in Table 1.

Table 1. Properties of FCC gasoline

	FCCG (full-range)	FCCG (60 °C +)
Density (g/cm ³ @15°C)	0.733	0.771
Sulfur (wtppm)	158.9	234.1
H/C (mol/mol)	1.93	1.83
Average molecular weight	102	112
GC-RON* ¹	90.5	88.9
Hydrocarbon type (vol%)* ¹		
Paraffins (P)	5.5	4.8
Isoparaffins (I)	37.6	32.4
Olefins (O)	26.3	19.7
Naphthenes (N)	9.2	12.4
Aromatics (A)	21.4	30.8

*1 Research octane number and hydrocarbon type were measured by GC.

Sulfide CoMo and NiMo catalysts were prepared by incipient wetness impregnation of γ -alumina with a mixed solution obtained from molybdenum oxide, cobalt (nickel) carbonate and a special ligand. All catalysts were presulfided in the stream of 5% H₂S/H₂ gas before reaction.

The selective hydrodesulfurization (HDS) of FCC gasoline was carried out in a high-pressure fixed-bed continuous-flow reactor. The reaction conditions were hydrogen pressure of 1~2 MPa, reaction temperature of 220~260 °C, liquid hourly space velocity (LHSV) of 4 h⁻¹, and a volume ratio of hydrogen (NTP) to feed of 100.

The hydrocarbon composition and research octane number (RON) in feedstock and products were analyzed by using PIONA-GC (Agilent 6890N (JIS K2536)-Yokogawa Analytical Systems Co. GPI system). The contents of total sulfur were measured by elemental analysis (Mitsubishi Chemicals Co., TS-100V). Sulfur compounds were analyzed by a GC-SCD (Agilent6890-Sievers355).

Results and Discussion

Figure 1 shows the time course of HDS percentage, olefin and aromatics hydrogenation percentage during HDS of FCC gasoline (60 °C+) for 56h. HDS activity showed almost constant, while olefin hydrogenation activity decreases drastically in the first 10h and

decreases gradually in the latter 46h. Aromatics hydrogenation activity showed zero except initial stage of reaction.

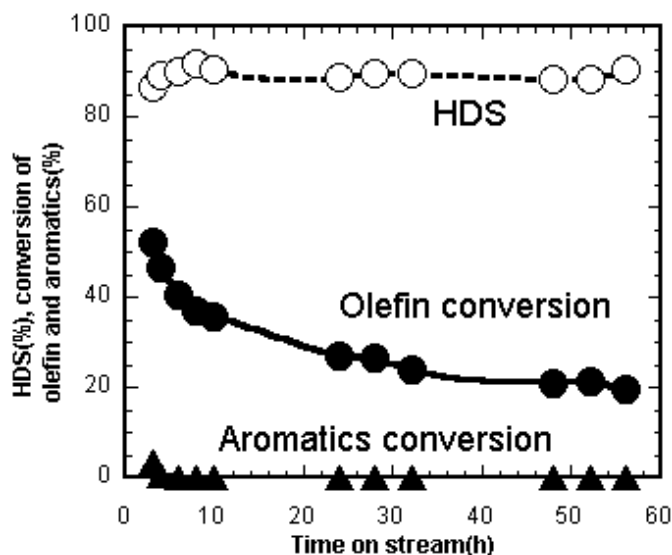


Figure 1. Time course of FCC gasoline (60 °C+)

hydrodesulfurization: Reaction conditions: temperature 240 °C; pressure 1MPa, LHSV, 4h⁻¹, H₂/feed ratio 100NL/L: Catalyst: CoMo/Al₂O₃ (CoO 3.1 wt%, MoO₃ 11.8 wt%)

Effect of catalyst species on properties of product oil in the hydrotreatment of heavy FCC gasoline is shown in Table 2. Both catalysts showed very high HDS activities. NiMo/Al₂O₃ catalyst gave a much higher olefin hydrogenation activity than CoMo/Al₂O₃ catalyst. This result means that CoMo/Al₂O₃ is more suitable for selective hydrogenation of FCC gasoline than NiMo/Al₂O₃.

Table 2. Effect of catalyst species on properties of product oil in the hydrotreatment of heavy FCC gasoline*¹

	FCCG (60 °C+)	NiMo/Al ₂ O ₃ * ²	CoMo/Al ₂ O ₃ * ²
Temperature(°C)	—	240	240
Time(h)	—	52	52
Density (g/cm ³ @15°C)	0.771	0.766	0.768
Sulfur (wtppm)	234.1	5.6	7.1
HDS (%)	—	97.6	97.0
Olefin conv.(%)	—	80.3	37.2
H/C (mol/mol)	1.83	1.87	1.85
Average molecular weight	112	112	112
GC-RON* ³	88.9	85.6	87.1
Hydrocarbon type (vol%)			
Paraffins (P)	4.8	9.6	7.3
Isoparaffins (I)	32.4	41.8	36.9
Olefins (O)	19.7	3.8	12.3
Naphthenes (N)	12.4	14.8	13.4
Aromatics (A)	30.8	30.1	30.1

*1 Reaction conditions: temperature 240 °C; pressure 2MPa, LHSV, 4h⁻¹, H₂/feed ratio 100NL/L

*2 NiO (CoO) 6.1wt%-MoO₃ 23.6wt%, sulfidation, 340 °C for 3h

*3 Research octane number measured by GC

Figure 2 shows effect of sulfidation temperature of catalyst on HDS and olefin hydrogenation activities. The reaction carried out at

220, 240 and 260 °C. It is noted that olefin hydrogenation activity of the catalyst sulfided at 319°C is much lower than those of other catalysts, while HDS activity showed almost same level. These results suggest that sulfidation temperature have much larger influence on olefin hydrogenation active sites than the HDS active sites. These phenomena appeared more remarkably at higher temperature. According to the proposed olefin hydrogenation active site, olefin hydrogenation occurs at Mo coordinatively unsaturated sites (CUS) (4). Perhaps, CUS Mo sites of this catalyst may selectively disappear.

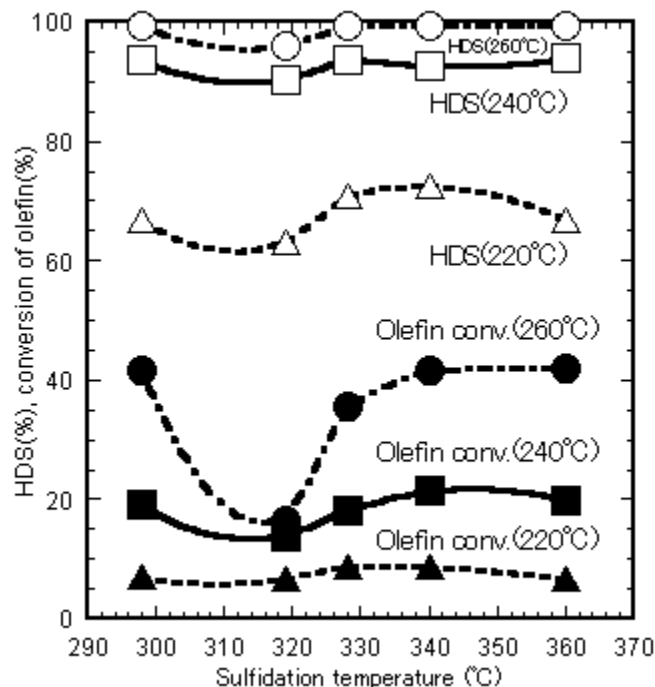


Figure 2. Effect of sulfidation temperature of catalyst on HDS and olefin hydrogenation : Reaction conditions: pressure 1MPa, LHSV, 4h⁻¹, H₂/feed ratio 100NL/L : Catalyst: CoMo/Al₂O₃ (CoO 3.1 wt%, MoO₃ 11.8 wt%)

Figure 3 shows HDS and olefin hydrogenation activity in the hydrotreatment of full-range FCC gasoline. Olefin hydrogenation activity of developed catalyst is relatively low and octane (GC-RON) loss is 0.6 to 1.3 in the range of 220°C to 260°C. However, olefin hydrogenation activity of commercial catalyst drastically increased at 260°C, while HDS activities of both catalysts showed almost same. From the analysis of various C5 and C6 olefin reactivity, terminal olefin hydrogenation activity for the developed catalyst (43.6~49.8%) showed slightly lower than the commercial one (48.2~59.6%). However, internal olefin hydrogenation activity at 260 °C for the developed catalyst (-18.2~5.0%) showed much lower than the commercial one (-17.6~23.6%). These results suggest that internal olefin is less active at olefin hydrogenation active site of developed catalyst. At lower temperature, conversion of internal olefin showed minus value because of formation of internal olefins from terminal olefins by C=C double bond isomerization. These phenomena are effective olefin hydrogenation depression.

Sulfur compounds in full-range FCC gasoline product oils were analyzed by GC-SCD. Benzothiophene and methylbenzothiophene were completely desulfurized. Most of sulfur compounds remaining in the product are thiophene and alkylthiophenes. Slight amounts of sulfur compounds such as 2-pentanethiol which were produced by re-

combination reaction between olefins and hydrogen sulfide were observed.

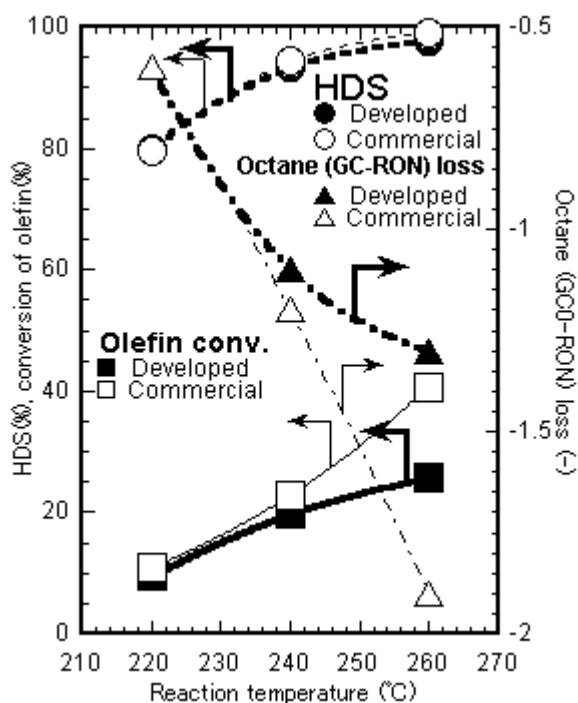


Figure 3. HDS and olefin hydrogenation activity in the hydrotreatment of full-range FCC gasoline: Reaction conditions: pressure 1MPa, LHSV, 4h⁻¹, H₂/feed ratio 100NL/L: Catalyst: CoMo/Al₂O₃ (developed, CoO 3.1 wt%, MoO₃ 11.8 wt%; commercial, CoO 4.5 wt%, MoO₃ 16.9 wt%)

Conclusions

The developed CoMo/Al₂O₃ catalyst showed high HDS activity and depressed olefin hydrogenation. The HDS selectivity of the catalyst depended on their sulfidation conditions. Olefin hydrogenation activity of the catalyst sulfided at 319°C less increased with increasing operating temperature than those of other catalysts. At higher temperature, internal olefin hydrogenation activity of the developed catalyst was much lower than that of commercial one.

References

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